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FC

HEAT RESISTANT EXPLOSIVES VI

PROPERTIES OF 1, 3–DIAMINO–2, 4, 6–TRINITROBENZENE, DATB

17 MARCH 1959

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

CONFIDENTIAL

HEAT RESISTANT EXPLOSIVES VI

Properties of 1, 3-Diamino-2, 4, 6-Trinitrobenzene, DATB

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ABSTRACT: 1, 3-Diamino-2, 4, 6-trinitrobenzene, DATB, decomposes at a rate of about 1 to 1.5% per hour at 260°C. Two polymorphs have been identified with a transition temperature of 217°C. Densities, X-ray powder diffraction patterns, and unit cell dimensions of the two polymorphs are reported. The infrared absorption spectrum and solubility data are also given.

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This report contains physical constants and properties of an experimental high temperature stable explosive, 1, 3-diamino-2, 4, 6-trinitrobenzene, DATB, which have been determined in the Organic Chemistry Division of the Chemistry Research Department. Other recent work on this explosive is covered in NAVORD Reports 6208, 6223 and 6225.

The work reported herein should be helpful in evaluating DATB for military applications, in developing analytical methods and in additional studies on the properties of DATB. Funds allocated under Tasks NOL 260 and 301-664/43006/08 were used for this project.

MELL A. PETERSON
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

1, 3-Diamino-2, 4, 6-trinitrobenzene, DATB, is a high melting explosive (286°C) which decomposes about 1 to 1.5% per hour at 260°C (500°F). Its density is slightly greater than that of RDX and it is somewhat less sensitive than TNT by the standard ERL drop-weight impact test. Considerable success has been achieved in the synthesis of DATB, (1), (2), (3), (4). Two efficient synthetic routes have been found as well as a semi-continuous modification of one, Figure 1.

This report contains a number of significant physical and chemical properties of DATB that have been determined by the Organic Chemistry Division.

POLYMORPHISM

Two crystalline forms of DATB have been observed. The low temperature form, I, transforms to a high temperature form, II, when heated above 217°C, the transition temperature. This polymorphic transition was discovered by microscopic observation and confirmed by X-ray diffraction. The transition temperature was determined by heating samples of form I for forty minutes at several different temperatures and finding which had transformed to form II by X-ray diffraction on powdered samples. The powder diffraction patterns of forms I and II are given in Table I. The impact sensitivity of form II, as determined by the standard ERL drop-weight impact machine, is the same as that of form I. Only form I has been obtained from the syntheses previously mentioned.

Form II DATB shows a pronounced tendency to persist in a metastable state below the transition temperature. One sample has been kept at room temperature for more than six months without transformation. Other samples of form II heated at 190°, 200°, and 210°C showed no signs of transformation after seven hours at these temperatures. A II ⟶ I solid-solid transition is thus improbable under any set of practical conditions likely to be encountered.

The DATB II ⟶ I solution phase transition takes place rather rapidly, however, under gamma-butyrolactone at room temperature. Crystals of form I are observed after about an hour and the transition is largely completed in four to six hours. The transition also takes place under acetone or dioxane but requires a longer period of time. The rate of a solution phase transition is a function of temperature, solvent, and particle size of the sample.

Purified DATB melts at 286°C. The melt solidifies to form II as would be expected. DATB sublimes readily at atmospheric pressure at 200°C, and excellent crystals of form II have been obtained by heating a few hours at this temperature. A concentrated solution of DATB in gamma-butyrolactone near its boiling point, when cooled rapidly, yields a mixture of large crystals of I and II.

DENSITY

Large well-formed crystals of DATB-I were used for a precise measurement of the crystal density by the flotation equilibrium method (5). A value of 1.837 (23°C) was obtained which is believed to be accurate within one part per thousand. The crystal density of DATB-II was found to be 1.815 by the same procedure. Therefore, the two polymorphs differ in density by about 1%.

HIGH TEMPERATURE STABILITY

DATB shows very good stability at 260°C. A majority of the batches synthesized on a semi-pilot plant scale produced about 4 to 6 cc of gas per gram of explosive per hour. Calculations based on the complete decomposition of a small weighed sample of DATB at 260°C show that one gram will yield 420 cc of gas. Thus, a typical sample of DATB decomposes about 1 to 1 1/2% per hour. At 260°C the rate of decomposition is approximately constant for at least six hours. On the other hand, at 280°C the rate of decomposition appears to be autocatalytic, Figure 2. In all probability decomposition products are accumulating in the DATB until the sample is molten at 280°C. The first part of the curve, Figure 1, therefore represents largely the rate of solid decomposition while the part after 100 minutes represents the rate of liquid decomposition.

SOLUBILITY

DATB is rather insoluble in methanol, acetone, benzene and hexane; slightly soluble in hot dioxane, nitrobenzene and glacial acetic acid; and relatively soluble in hot gamma-butyrolactone as shown below.

Temperature, °C	g/100 ml gamma-butyrolactone
100	5
125	10
150	25

INFRARED ABSORBTION SPECTRUM

Table II lists the wavelengths, relative intensities, and, when possible, the assignments of the absorption maxima in the spectrum of DATB-I. The spectrum was obtained from a sample which had been recrystallized three times from gamma-butyrolactone. The solid was run as a Nujol mull in the region 680-1320 cm^{-1} and as a Fluorolube mull in the region 1300-5000cm^{-1} on a Beckman IR 4 equipped with sodium chloride prisms. The only extraneous band due to the dispersing agent occurs at 730 cm^{-1}. The frequencies for NH stretching and deformation are normal. Two nitro group stretching bands are found, the asymmetrical band at 1555 cm^{-1} and the symmetrical band at 1359 cm^{-1}.

UNIT CELL DIMENSIONS

The unit cell dimensions of crystals of both DATB-I and DATB-II have been determined by X-ray diffraction using the Weissenberg method. The DATB-I crystal used for these measurements was a rectangular shaped rod obtained by recrystallization from gamma-butyrolactone at moderate temperatures. The DATB-II crystal was selected from a mixture of form I and form II crystals obtained by rapid crystallization of DATB from boiling gamma-butyrolactone. It was a thick plate roughly hexagonal in shape. This DATB-II crystal proved to be a twin, and thus the data given below for DATB-II may not be as reliable as that given for DATB-I.

Crystal Symmetry	DATB-I Monoclinic	DATB-II Monoclinic
a axis, Å	7.26	7.76
b " , Å	5.21	9.04
c " , Å	11.68	12.84
β, degrees	96	103
Unit cell volume, $Å^3$	440	877
Molecules per unit cell	2	4
Calculated density, g/cc	1.835	1.84
Measured density, g/cc	1.837	1.815
Probable space group	P c	

ACKNOWLEDGMENT

The authors acknowledge the assistance of T. N. Hall who performed the infrared measurements and of H. T. Simmons for the crystal density measurements.

Table I

X-Ray Powder Diffraction Patterns of DATB-I and DATB-II

DATB - I			DATB - II		
d Å	Relative Intensity	2θ CuK_α	d Å	Relative Intensity	2θ CuK_α
7.25	90	12.2	7.55	14	11.7
5.79	53	15.3	7.13	6	12.4
5.18	4	17.1	6.06	10	14.6
4.79	22	18.5	5.47	7	16.2
4.33	98	20.5	5.37	10	16.5
4.23	20	21.0	4.41	17	20.1
4.04	27	22.0	4.25	23	20.9
3.88	37	22.9	3.97	10	22.4
3.63	27	24.5	3.69	14	24.1
3.52	92	25.3	3.60	11	24.7
3.23	22	27.6	3.45	4	25.8
2.94	100	30.4	3.41	4	26.1
2.80	12	31.9	3.12	100	28.6
2.60	8	34.4	2.93	7	30.5
2.56	10	35.0	2.81	3	31.8
2.46	10	36.5	2.72	3	32.9

Table I (cont'd)

X-Ray Powder Diffraction Patterns of DATB-I and DATB-II

DATB - I			DATB - II		
d Å	Relative Intensity	2θ CuK$_\alpha$	d Å	Relative Intensity	2θ CuK$_\alpha$
2.27	2	39.7	2.61	3	34.3
2.19	16	41.1	2.55	3	35.2
2.16	31	41.8	2.13	13	42.5
2.12	14	42.6	2.10	10	43.1
1.99	10	45.5			

Table II

The Infrared Absorption Spectrum of DATB-I

Wave Number cm^{-1}	Intensity	Assignment
783	M	C-H out of plane deformation
832	W	
896	W	C-H out of plane deformation (para-substituted benzene)
1030	W broad	
1215	M broad	
1308	M	C-N stretching (aromatic primary amines)
1355	M broad	Nitro group - symmetrical stretching
1475	W broad	C=C stretching
1520	W	
1555	W	Nitro group - asymmetrical stretching
1602	S	N-H deformation (primary amines)
2930	W broad	
3270	M	N-H stretching (primary amines)
3375	M	N-H stretching (primary amines)

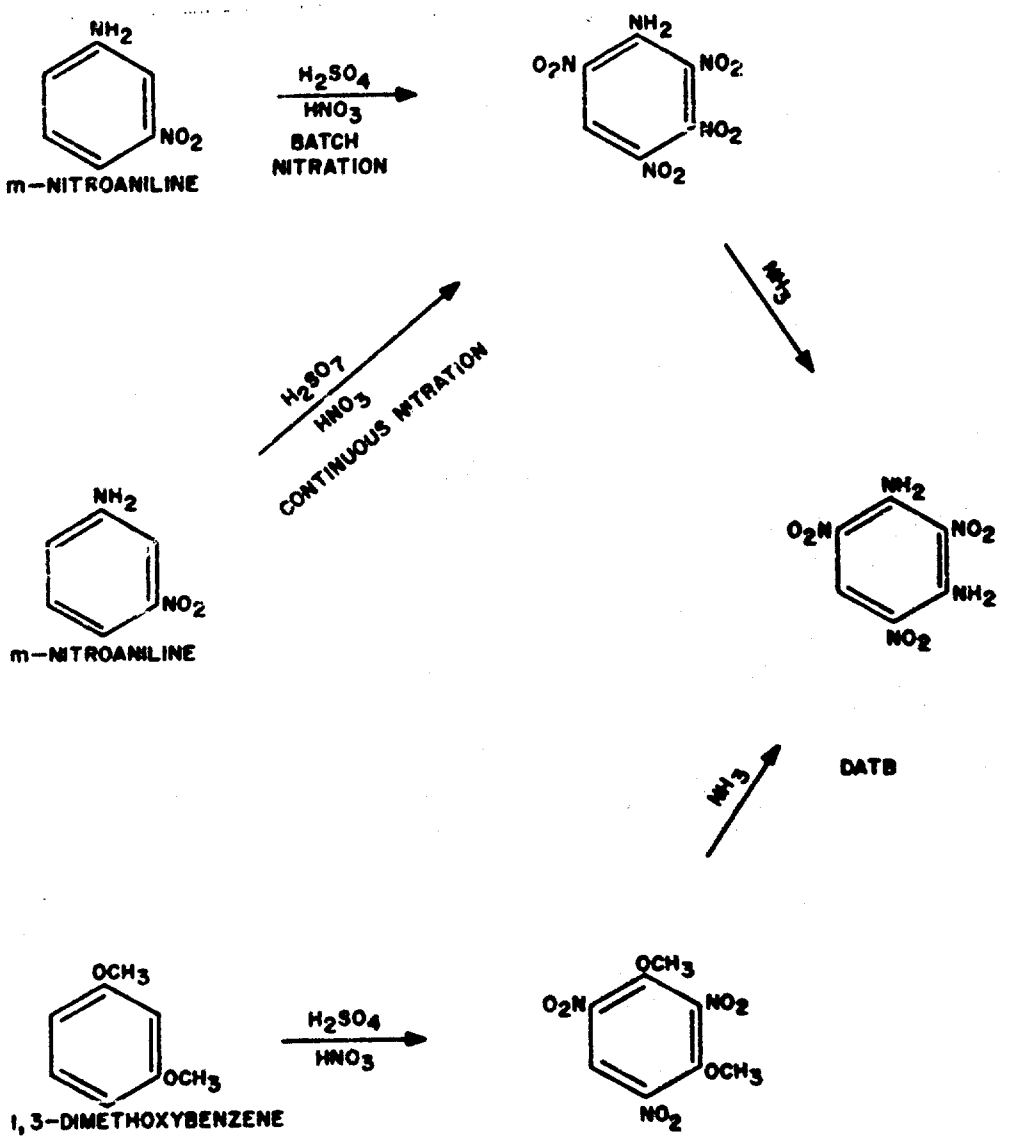

FIG. 1 SYNTHESIS OF DATB

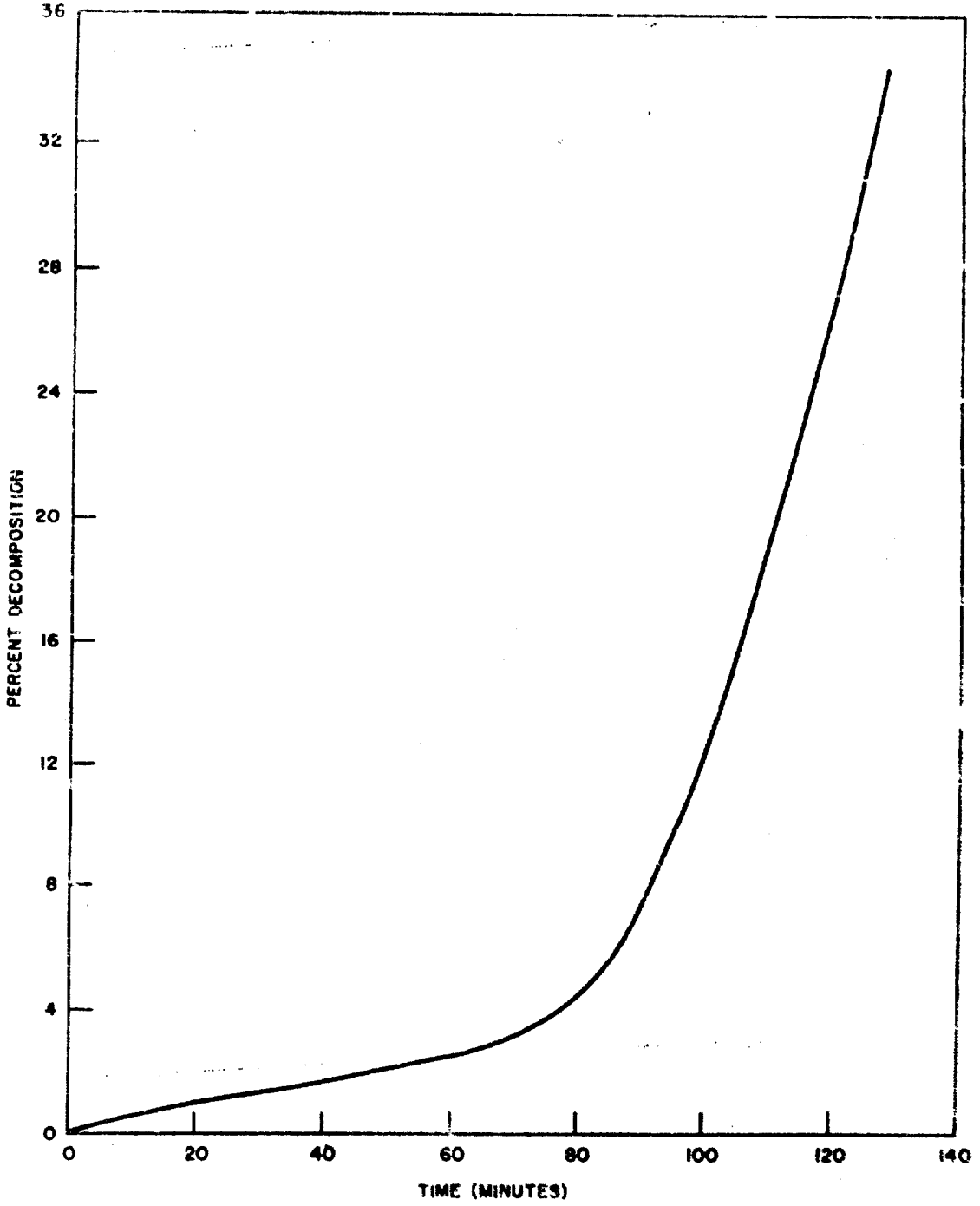

FIG. 2 DECOMPOSITION OF DATB AT 280° C

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